

Ionic Size in Relation to the Physical Properties of Aqueous Solutions.

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(Abstract.)

The electrical conductivity of a solution depends upon the rates of transference of the ionised portions of the solute in opposite directions under the influence of the applied electromotive force. These rates of transference under a given potential gradient are conditioned by the viscosity of the medium, and the sizes and possibly the shapes of the ions. Increase of viscosity of the solution and increase in the sizes of the migrating ions both tend to diminish the rates of transference of the ions, and thus to lower the conductivity. If the ion enters into combination with one or more molecules of water, its size is necessarily increased, and the motion of the water-logged ion becomes more sluggish as the amount of water in combination increases. To separate the elements which determine the conductivity of an electrolytic solution, and to analyse the joint effect of variations in ionisation, viscosity, and water combination is a matter of great difficulty, but of much importance to the theory of solution.

In a former paper (Bousfield on "Ionic Sizes in Relation to the Conductivity of Electrolytes")* was proposed a method for effecting such an analysis based upon the expression evaluated by Stokes for the terminal velocity of a small sphere moving in a viscous medium. A consideration of the influence of the water in combination with the ion upon its mobility was used to obtain a correction of the coefficient of ionisation which made Van't Hoff's law (in a slightly modified form) an *accurate* expression of the relation between ionisation and dilution, down to twice decinormal solutions of KCl. This method of procedure gave for the radius of the hydrated ion an expression of the form

$$r = r_{\infty}(1 + Bk^{-3})^{-1},$$

which indicated that the average radius of the ion steadily increased with dilution, owing to increasing hydration of the ion, up to "infinite dilution."

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Whether the resulting expression for r did in fact represent the average radius of the ion was tested by a consideration of the density law which would thence result. The volumes of the ions would be proportional to r^3 , and it was found that a rational density formula could be constructed upon this basis which accurately corresponded with the observed densities of the solutions.

In the present paper, the necessary experimental determinations for applying the method to solutions of NaCl are given, together with some other determinations for collateral purposes, and the hypothesis is further tested by reference to other physical properties of solutions. These results are independently of some value, apart from the hypothesis by which they are reached, and it has been thought well to designate the function r , which, according to our view, expresses the average radius of the ion, by the term "radion." Whilst this term connotes our hypothesis, it may, if necessary, be merely considered as expressing a certain function of the dilution. But it has a further convenience as it enables us readily to extend the conception to denote the average molecular radius of any group of ions or molecules, or even of the whole of the ions and molecules both of solvent and solute in any given solution. The utility of this extended conception will appear more clearly in the section relating to a consideration of ionic size with reference to the viscosity of a solution.

The volume of the ion, according to our hypothesis, is proportional to the cube of the radion, and the volume of a pair of ions to the sum of the cubes. These cubes and their sums we refer to as "ionic volumes." But, except where the context indicates the contrary, the term "radion" may be taken as merely denoting the function

$$r = r_{\infty}(1 + Bh^{-\frac{2}{3}})^{-1},$$

and the term "ionic volume" as denoting the cube of the radion or sum of the cubes of the radions, apart from the hypothesis as to size.

As in our former paper with reference to KCl, it is shown that the "solution volume" of NaCl solutions is a linear function of the ionic volumes. Hence the densities of KCl and NaCl solutions can both be accurately expressed by the same formula, as simple functions of the radions.

A theoretical consideration of the relation of the Hittorf migration numbers to the sizes of the ions is given, and it is shown that our hypothesis as to the influence of ionic sizes upon rates of transference, would theoretically lead to the result that the reciprocals of the Hittorf migration numbers should be expressible as a linear function of the ratio of the radions. This turns out, in fact, to be the case, and we incidentally

arrive at a useful method of extrapolation to determine the value of the Hittorf number for an electrolyte at "infinite" dilution.

These considerations enable us to determine the coefficients B for the separate ions in the expressions for the radions. These coefficients B we refer to as the "hydration numbers," the relation between the hydration numbers and the migration numbers at infinite dilution being of the form—

$$B = B_1N_1 + B_2N_2.$$

Turning now to a consideration of the viscosities of the KCl and NaCl solutions, it is shown that the viscosity of dilute solutions can be represented approximately as a linear function of the radions, as can also the viscosity of mixtures of normal KCl and NaCl solutions.

Passing to a consideration of the general relation of viscosity to ionic size, the extended conception of the radion is introduced, and an approximate value is given to the radion of water, which expresses the average radius of the water molecules reckoned upon the same scale as the radions of the solute. Using this value of the water radion in conjunction with the values of the radions of the solute determined from the conductivities, it is shown that the viscosity of the solutions can be expressed with a fair approach to accuracy by the expression

$$\eta = C\Sigma\beta r,$$

where r stands for the radion of a given species of molecules and β for the fraction of the total volume occupied by such species. Since $\Sigma\beta r$ is, upon the extended conception of the radion, the average molecular radius of the whole solution, we may express this result by saying that the viscosity of a solution is proportional to its radion.

In order to correlate ionic sizes with osmotic pressure a prolonged attempt was made to measure the vapour pressure of dilute KCl solutions at 18° C. A large barometer tube was used, closed by a small tap at the bottom, so that minute differences of level could be determined by removing and weighing the mercury cistern. A similar arrangement was used to determine simultaneously the variations of atmospheric pressure during each observation. It was found, however, that the variations of atmospheric pressure were often larger than the differences of vapour pressure to be measured, and no sufficiently accurate results could be obtained. Recourse was therefore had to the freezing-point determinations of Jahn with KCl and NaCl solutions. The variations of ionic size with temperature are probably serious and at present* unknown, and hence a consideration of ionic sizes

* In my former paper I attempted to calculate the variation of ionic size with temperature by reference to the conductivity temperature coefficients of the ions at infinite

at 18° C. in relation to osmotic data at another temperature might lead to error. But it seemed probable that the ionic sizes at different dilutions might have the same *relative* values at 18° C. and 0° C., and in the absence of other data it was decided to use these.

Defining the "effective molecular freezing-point depression" as the ordinary so-called molecular freezing-point depression divided by $(1 + \alpha)$, where α is the ionisation, and denoting it by the letter D , it was found that D was a linear function of the ionic volume, and that it could be expressed both for KCl and NaCl as

$$D = 1.86 + C(I_{\infty} - I_v),$$

where I_v stands for the ionic volume at the given dilution and I_{∞} for the ionic volume at infinite dilution, the value of the constant C being nearly the same for both substances.

In addition to the confirmation thus afforded to our view as to the fundamental importance of the radion in the theory of solutions, we are further led to a useful formula for obtaining by extrapolation the value of the molecular freezing-point depression at "infinite" dilution. For this purpose we are able to dispense with our hypothesis, and obtain from it a new result quite independent of it—one of the recognised tests of the validity of a hypothesis, though not a conclusive one.

We saw that the solution volume was a linear function of the ionic volume, and we have now the effective molecular freezing-point depression also as a linear function of the ionic volume. Hence the effective molecular freezing-point depression should be a linear function of the solution volume, and in this case the reference to ionic sizes which correlated the two sets of phenomena can be dispensed with. In order to test this matter, measurements of the densities of KCl and NaCl solutions at 0° C. were made. This is a little above the freezing point of dilute solutions, but it was considered to be near enough to make the desired comparison. Density measurements were made upon solutions of strengths of 1/2, 1/4, 1/8, 1/16, and 1/32 normal, and empirical formulæ (based on the lines of the rational formulæ for 18° C.) were constructed to obtain the solution volumes at the concentrations at which Jahn's freezing-point determinations were made.

dilution which were given by Kohlrausch. I have, however, since come to the conclusion that these results are unreliable. Kohlrausch's values were largely based on determinations of the conductivities of 1/1000 normal solutions. Dissociation being incomplete in such solutions, any variation of conductivity due to change of ionisation with temperature would be included in his temperature coefficients and might entirely vitiate the deductions which I drew. This portion of my former paper must therefore be withdrawn, and I propose to pursue the matter further experimentally

The result was that the effective molecular freezing-point depression, both for KCl and NaCl solutions, could be expressed by one formula with the same constants for both substances, viz. :—

$$D = 1.86 + 3.3\delta V_s,$$

where δV_s is the change in the solution volume for different dilutions. This formula would also include a non-electrolyte such as sugar, in which δ is almost zero.

In this sketch of the course of the present paper, we have passed over some matters arising incidentally which may call for mention. But it must be observed that the main purpose kept in view throughout, is to show the interpenetration of the theory of ionic sizes with the theories of the various phenomena of solutions, and to test the theory as far as possible in its relation to such phenomena. In this process various side avenues have been opened up, which we have forborne to follow if they carried us too far from the main track.

One incidental matter of importance is the correction of the coefficient of ionisation which is afforded by the theory, according to which the true value of the coefficient of ionisation is

$$\alpha = \frac{\lambda}{\Lambda} \cdot \frac{\eta}{1 + B\eta^{-\frac{2}{3}}}.$$

The result of this correction is to make the values of α for KCl and NaCl *identical* for equimolecular solutions, down to twice decinormal concentration. An accurate empirical formula for α was proposed by Kohlrausch* of the form

$$\frac{1-\alpha}{\alpha^p} = Cm^{\frac{1}{2}}.$$

The values of the constants given by Kohlrausch were :—

	<i>p.</i>	<i>C.</i>
KCl	3.280	0.7190
NaCl	2.649	0.7707

Thus two sets of different constants are required to give the values of α for the two substances at the same concentration. The values of the constant p for the two substances differ by about 20 per cent. The resulting values of α at twice decinormal concentration differ by about 3 per cent. Our values of α , which are corrected for size of ions and viscosity of solution, being identical, are given by one formula with the same constant for KCl and NaCl, viz. :—

$$\frac{h}{\alpha} \left/ \left(\frac{h}{1-\alpha} \right)^{\frac{2}{3}} \right. = 3.197.$$

* 'Sitz. der K. Preuss. Akad. der Wiss. zu Berlin,' vol. 44, p. 1002, 1900.

This matter was further tested by determining the densities of mixtures of normal solutions of KCl and NaCl, and it was found that the observed densities were correctly given by the "law of mixtures" within very narrow limits.

The conductivities of these mixtures were also determined and a mixture law for the conductivities based upon the consideration of viscosities and ionic sizes was formulated. The agreement thus obtained between observed and calculated values also tends to show that the hypothesis upon which the calculations were made is correct.

The increase in the ionic volumes which takes place with increasing dilution must be nearly proportional to the increasing volume of water combined with the ion. The development of this matter quantitatively so as to determine the number of molecules of water in combination with the ion under different circumstances is a matter of great importance, but it cannot be dealt with in this paper. The effect of water combination as a sufficient and possibly the only cause of ionisation, is dealt with, to some extent, in the former paper,* and has also recently been considered by Lowry (An Application to Electrolytes of the Hydrate Theory of Solution).†

Concluding Observations.

Let us now briefly review the main course of the argument, as developed in this and the former paper, in relation to our fundamental hypothesis.

As our starting point we took the Van't Hoff dilution law, which we may express by saying that if D represents the concentration of the dissociated portion of a solute and U the concentration of the undissociated portion, reckoned by means of the ordinary value of α , there exists a linear relation between $\log D$ and $\log U$, leading to a relation of the form $K = D/U^n$, where n is for various electrolytes nearly but not quite two-thirds. (For KCl $n = 2.2/3.2$ about.)

This suggested that if we could find a suitable correction for α , which is usually taken as λ/Λ , the Van't Hoff dilution law would turn out to be an *exact* relation for dilute solutions of binary electrolytes such as KCl.

The materials for such a correction were sought in the known fact that the viscosity of the solution produced aberrations in the mobilities of the ions, but viscosity differences alone were inadequate to give an account of such aberrations.

Kohlrausch's observations on the temperature coefficients of the ions had

* See the revised version published in the 'Zeitschrift f. Phys. Chem.,' *loc. cit.*

† 'Trans. Farad. Socy.,' vol. 1, p. 197, 1905.

already led him to the general view that the ions must be considered to be water-coated.* This water combination necessarily altered the sizes of the ions, and it was considered that the joint effect of changes of viscosity and changes of size might adequately account for changes in the mobility.

To reckon these effects quantitatively, Stokes' theorem as to the motion of a small sphere in a viscous medium was available, and though the actual motion of the ions through an electrolyte under the influence of a potential gradient is probably extremely erratic, it was thought that, nevertheless, the effect of size and viscosity upon the average rectilinear drift under the influence of the electromotive force might be amenable to exact treatment, just as the average rectilinear drift itself can be accurately calculated.

Assuming, then, that the aberrations of the mobilities which made the Van't Hoff law inexact were due to such causes and could be dealt with in this way, corrections were applied to the mobilities and corrections for α were calculated, the nature of which was determined by the Stokes theorem, and the amount of which was determined by the Van't Hoff law (expressed in terms of the hydration h instead of the volume V of the solution).

The result of this process was to give us the expression

$$r = r_{\infty}(1 + Bh^{-\frac{2}{3}})^{-1}$$

for the relation between the radius of an ion and the dilution of the solution.

Up to this point, if one may compare small things with great, the process followed is similar to that of the astronomer who sought to locate the position of a new planet by considering the irregularities produced in the movements of the old ones. In that case the result could be tested by turning a telescope to the spot indicated by the calculations.

In the present case the result could only be tested by considering how far the hypothesis as to the changing sizes of the ions owing to the changes in the amount of water combination could be rationally related to the various physical phenomena of solutions, and how the quantitative results were functionally related to existing data. In the case of each set of phenomena it was necessary to consider *à priori* how the changing size of the ions would be likely to affect it.

A priori it seemed probable that the Hittorf transference numbers, and the viscosities of the solutions themselves, would depend merely upon the linear dimensions of the ions, whilst the densities of the solutions and the variations of effective molecular freezing-point depression would depend upon

* 'Roy. Soc. Proc.,' vol. 71, 1903, p. 338.

the amounts of combined water, and therefore upon the cubes of the ionic dimensions.

These *à priori* considerations have, in fact, turned out to be justified, not merely qualitatively, but with considerable numerical accuracy, having regard to the difficulty of some of the approximations involved. We are able to express the Hittorf numbers, the densities, and the effective molecular freezing-point depressions within the limits of experimental error, as simple functions of the radions, and to express the viscosities with a fair approach to accuracy, not merely as a function of the radions of the solute, but also upon the extended conception of the radion, as being simply proportional to the radion, or average molecular radius, of the whole solution. Our hypothesis has also enabled us to predict two new relations which are independent of the hypothesis, viz., the fact that the Hittorf migration numbers are a linear function of $(B + k^{-3})^{-1}$ and the fact that the effective molecular freezing-point depression is a linear function of the solution volume.

It is submitted that the above considerations justify the working hypothesis that the function which we have named the radion, derived as above described, may in fact be taken to be a measure of the actual sizes of the ions. In any case the radion turns out to be of fundamental importance in correlating the various phenomena of solution.
